



Electrochemical polishing of Ti–13Nb–13Zr alloy

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ABSTRACT

This work presents the results of the investigations on electropolishing of the Ti–13Nb–13Zr titanium alloy. The electropolishing was conducted in the solution containing ammonium fluoride and sulfuric acid. The influence of electropolishing process parameters on the texture (AFM, SEM) and chemical composition (EDX, XPS) of the surface layer was established. The Ti–13Nb–13Zr alloy after the electropolishing is covered with a thin layer composed mainly of titanium, niobium and zirconium oxides. Electrochemical impedance spectroscopy in 5% NaCl solution was used for the determination of the corrosion resistance of the alloy. The application of the electropolishing increases the corrosion resistance of the Ti–13Nb–13Zr alloy significantly. The increase of the corrosion resistance of the alloy is connected with the smoothing of the surface and with the formation of Ti, Nb and Zr oxides layer on the surface.

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1. Introduction

Titanium and its alloys find many important applications. Because of many advantageous properties they are used in aeronautics, automotive industry, extreme sports, as well as in the jewelry and biomedical engineering. The titanium alloys are used, among other things, for the production of joint endoprosthetics, as elements for joining bone fractions, as components of heart valves and artificial hearts in cardiac surgery and interventional cardiology and for medical instrumentation [1–4]. Such titanium alloys as Ti–6Al–4V, Ti–6Al–4V ELI, Ti–6Al–7Nb find the widest application in prosthetic engineering [5]. However, these alloys contain carcinogenic vanadium and allergenic aluminum [6–12]. The alternative material is Ti–13Nb–13Zr. This alloy is highly resistant to corrosion, has low value of the Young module and good biocompatibility, which makes it possible to use in the bone, joint and dental prosthetics [13].

No implanted metal elements that have not been earlier surface treated are used in the medical practice. One of the appropriate treatment methods is electrolytic polishing. The electropolishing produces microscopically smooth surfaces, free of stress and occlusions, most often of the “mirror” glance. Moreover, the corrosion resistance of the polished part is increased and its surface is microbiologically clean (hydrogen is removed from the surface, which hinders the growth of bacteria) [14]. The electropolishing produces surfaces completely free of deformations preserving the original lattice structure. The degree of

smoothing is greater when the structure and chemical composition of the alloy are more uniform [15]. The electrolytic polishing of titanium and some of its alloys has been described in many papers [16–41]. It was found that this process affects advantageously the corrosion resistance of titanium and its alloys. The baths most commonly used in the electropolishing of titanium and its alloys are based on:

- perchloric acid, HClO₄ [19,21],
- normal alkanols, such as methanol, ethanol, and n-butanol with additives [19,22–26],
- hydrofluoric acid and sulfuric acid (VI) [28–31,42],
- sulfuric acid (VI), hydrofluoric acid and acetic acid [17],
- sulfuric acid (VI), hydrofluoric acid and nitric acid (V) [18].

These baths are often explosive or require low temperature of operation. On the other hand, there is no information on the electrolytic polishing of the Ti–13Nb–13Zr alloy.

We present the results of the electrolytic polishing of the Ti–13Nb–13Zr alloy for the first time. We have determined the effect of the electropolishing parameters on the surface morphology and chemical composition (SEM, AFM, EDX, XPS) and corrosion resistance in sodium chloride solution (EIS).

2. Experimental

The Ti–13Nb–13Zr alloy (BIMO Metals, Wrocław, Poland) used in this investigations had the composition presented in Table 1. The samples of that alloy had a cylindrical shape with a diameter of 9.5 mm and a

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Table 1

The chemical composition of the Ti–13Nb–13Zr alloy (wt.%).

Nb	Zr	N	C	H	Fe	O	Ti
13.30	13.00	0.009	0.05	0.005	0.08	0.1	Balance

height of 7 mm. They were ground using #320 and #600 abrasive papers (SiC) and then cleaned 5 min in an ultrasonic wash in 2-propanol and deionised water (sample TNZ). Afterwards, the samples were polished electrochemically.

The electropolishing was carried out in a 1 dm³ plastic electrolyzer, with a cover, two cathodes made of the acid-resistant steel and an anode clamp for fixing the samples [31]. The process was carried out with the use of the Unitra 5352M power supply. The current intensity and voltage on the electrolyzer clamps were measured with the LM-3 gauges, with an accuracy of ± 0.1 A and ± 0.1 V. The solution temperature (25 ± 0.1 °C) was maintained with the UH-4 thermostat. The Ti–13Nb–13Zr alloy samples were polished in the bath composed of 12.5 M sulfuric acid, 5.5 M ethylene glycol, and 2.7 M ammonium fluoride. The influence of current density and electric charge on the quality of the samples was studied following Table 2. The current efficiency was calculated basing on the weight loss during electropolishing. For the efficiency calculations maximal dissolution valency of the alloy components was used (Nb–V; Ti and Zr–IV).

The mean roughness factor Ra of the surface was measured using the profilometer SJ-301 (Mitutoyo) whereas the morphology of sample surfaces was studied using the high resolution scanning electron microscope Inspect F and the atomic forces microscope NanoScope E (Digital Instruments). The chemical composition of the selected samples was determined with EDX (Oxford Instruments attached to SEM) and XPS (Multitechnique Electron Spectrometer PHI 5700/660 from Physical Electronics). XPS spectra were measured using the monochromatic Al-K α radiation (1486.6 eV), employing a cylindrical mirror analyzer with an energy resolution of about 0.3 eV.

Spectroscopic ellipsometric measurements were performed using the EP3 ellipsometer from Nanofilm. The range of wavelength was 360–1001 nm and the angle of incidence was 80°. To calculate the thickness of the oxide the EM–Bruggemann model was used.

The electrochemical measurements were performed with the IM5d Impedance Spectrum Analyzer (Zahner Elektrik, Kronach, Germany). Samples were molded in an epoxy resin with wire connections attached in such a manner that only one circular flat surface was exposed to solution. Measurements were performed in the 5% NaCl solution. The frequency range used in the EIS measurements was 0.00655 to 100,000 Hz. The amplitude of sinusoidal voltage signal was 5 mV. A glass cell in three electrode configuration was used. A platinum foil was used as a counter electrode and an Ag|AgCl electrode in saturated KCl solution was used as a reference electrode. All potentials in this paper were given with respect to that electrode. During the measurement solution was stirred with a magnetic stirrer with a rotation speed

Table 2

The influence of the electropolishing parameters on the roughness of the Ti–13Nb–13Zr alloy; the cell voltage: 25–30 V.

Sample no.	$i/A \cdot dm^{-2}$	τ/min	$Q/A \cdot h$	$R_a/\mu m$
1	40	5.0	0.12	0.15
2	50	4.0	0.12	0.17
3	60	3.5	0.12	0.16
4	50	2.9	0.08	0.27
5	50	3.4	0.11	0.21
6	50	4.4	0.14	0.19
8	50	6.2	0.17	0.17

of 15 Hz. All EIS spectra were measured at the spontaneously established corrosion potential. The first spectrum was recorded just after sample immersion in the solution every 2 h and then less frequently during one month. The time of the acquisition of the spectrum was approximately one and a half hour.

All the solutions were prepared using analytical grade reagents from POCh Gliwice, Poland, and deionized water obtained from the Millipore-Q system.

3. Results and discussion

Fig. 1 presents SEM and AFM of the polished sample of the Ti–13Nb–13Zr alloy, of the roughness index Ra 0.27 μm , as measured with the profilograph. That Ra value measured over relatively large macroscopic area of 2 mm length includes characteristic scratches formed on the surface before and during the polishing. The Ra index measured for small microscopic, scratch free areas that was calculated based on the AFM results is much lower. For the image of $5 \times 5 \mu m$ area shown in Fig. 1b it is equal to 39.35 nm, which was found to be representative at microscopic scale. The difference between the real and geometric surface of the polished alloy reaches about 9%.

The values of the macroscopic roughness indexes Ra, change slightly with the increase of the current density from 40 to 60 A $\cdot dm^{-2}$ at fixed

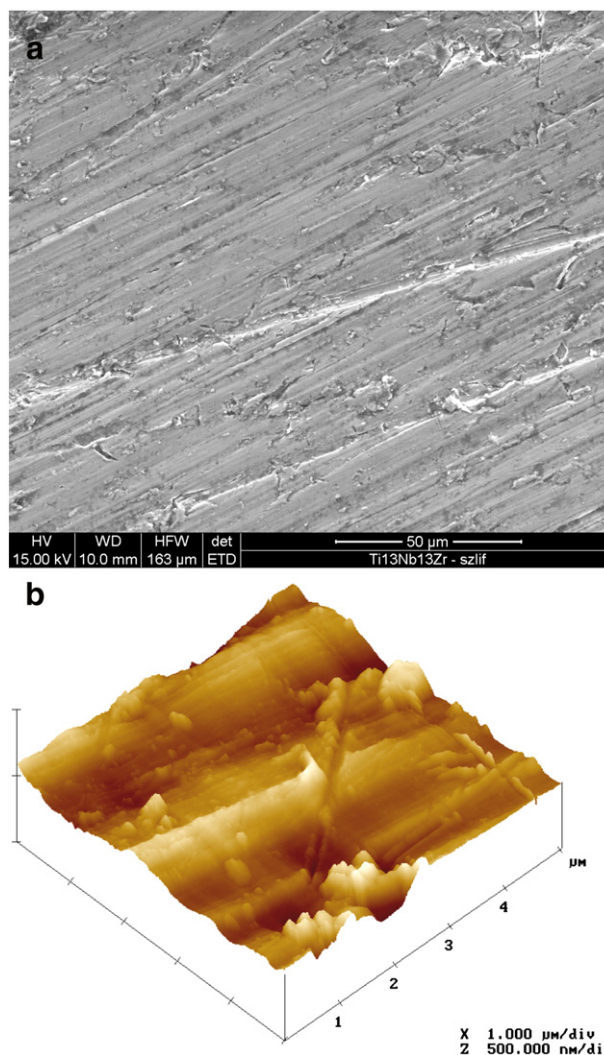


Fig. 1. The SEM (a) and AFM (b) images of the Ti–13Nb–13Zr alloy surface after grinding.

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